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PHYSICAL PROPERTIES OF MIXED PHOSPHATES OF COBALT AND NICKEL WITH THORIUM

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INTRODUCTION

Synthesis of mixed phosphates $MTh(PO_4)_2$, where M=Co(II) and Ni(II), is performed, and then a series of investigations of these compounds is performed. These compounds have not been described in literature so far. There are data on thorium phosphate compounds with the same general formula but with metals which have M(II) ions of higher ionic radius /1/.

SYNTHESIS

Synthesis of these compounds has been realised starting from water solution of Th-nitrate, M(II)-nitrate and sodium phosphate in stoichiometric ratio /2,3/. By adding acid /HCl/, precipitation started only from a very concentrated solution. By gradual heating and intensive stirring as well as slight temperature raising for 90 h, the temperature of 1250°C is achieved. With slow cooling homogeneous polycrystalline samples are obtained and used in the research described in this paper.

CRYSTALLOGRAPHIC DATA

Pulverised specimens of synthetized compounds are tested by x-ray diffractometry. It has been found out that both compounds crystallize in the monoclinic system matching the unit cell parameters stated in Table 1.

Table 1.

compound	unit cell parameters			
	a(nm)	b(nm)	c(nm)	β(°)
$CoTh(PO_4)_2$	0,6200	0,6443	0,5534	98,5
$NiTh(PO_4)_2$	0,6137	0,6287	0,5689	98,6

OPTICAL SPECTRA

The synthetized compounds are investigated by the method of a diffuse reflectance spectroscopy. Spectra recording is carried out at a room tempe-

rature in relation to $BaSO_4$ as reference sample. The range covered is from 357nm to 2500nm (i.e. $2{,}8.10^4 cm^{-1} + 4.10^3 cm^{-1}$). The spectra recorded are shown in Fig.1; the courves plotted represent socalled Kubelka-Munk's function /4/. The form of the spectra obtained indicates, according to characteristical literature samples /5,6/ that these spectra are of a crystal /ligand/ field of Co(II) and Ni(II)-ions in octahedral surrounding. Precisely, wide spectral bands within the range of 7000 cm^{-1} indicate that both octahedral surroundings are deformed /5,6/, but spectroscopy cannot reliably precise the deformation character. The analysis of these spectra is made by applying König-Kremer's diagrams /7/ and the appropriate analytical relations /5,6/. Estimated posilions of spectral lines are indicated in Fig.1. with arrows and calculated parameters are given in Table 2.

Table 2.

compound	crystal field parameters		
	10Dq(cm^{-1})	B(cm^{-1})	$\beta = B/B_o$
$CoFe(PO_4)_2$	6800	825	0,85
$NiFe(PO_4)_2$	7090	905	0,87

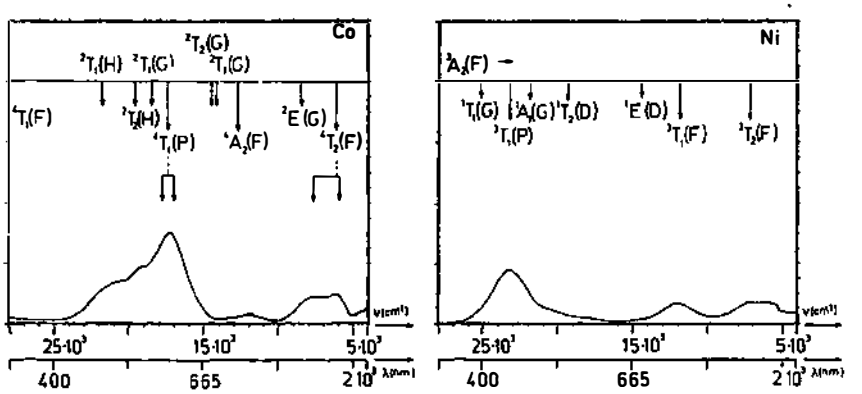

Fig.1.

MAGNETIC, DIELECTRIC AND ELECTRIC MEASUREMENT

Determination of temperature dependence is made within a wide temperature range for:

a. Magnetic (mass) susceptibility (χ_m) by Gouy method; measuring results are shown in Fig.2.;

b. Dielectric (relative) permittivity (ε_r) by a high-frequency measuring bridge (at 1 MHz); measuring results are given in Fig.3.;

c. Specific electric resistivity (ρ) by electrometric method; results are given in Fig.4.

Measurements under b. and c. are performed on pellets made of powder pressed under 5 MPa pressure. Briefly, general forme of temperature (T) dependence of $1/\varkappa_m$, ε_r and $\ln\rho$ is typical for paramagnets, linear dielectrics and for systems with weak electronic conductivity. But, certain discontinuities appear on these lines, indicating the change in the form of the temperature dependence. They correspond to structural phase transitions in the investigated phosphates. The mean temperatures of 3 observed phase transitions for Co-compound are equal to 400K, 545K and 715K, while the appropriate temperatures for Ni-compound are identical to 450K, 560K and 750K.

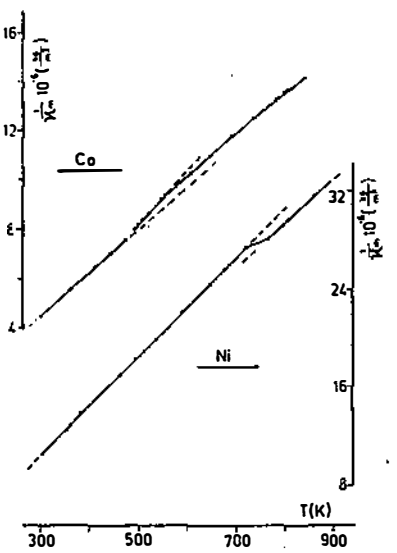

Fig.2.

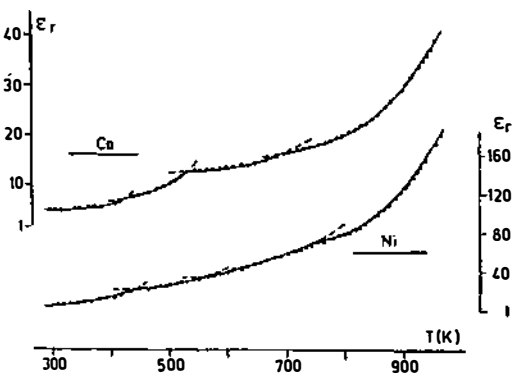

Fig.3.

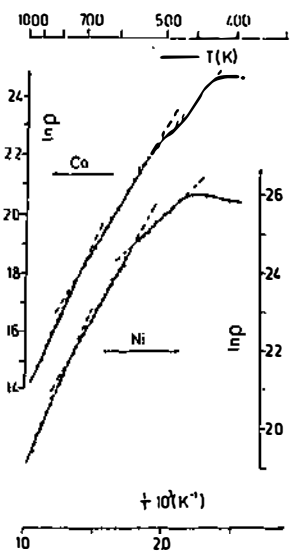

Fig.4.

CONCLUSION

Two new mixed phosphates are synthetized and studied. Crystal symmetry, crystallographic parameters, type of coordination surrounding of M(II) ions and crystal field parameters are determined. General behaviour of macroscopic parameters is also established, as well as the existence of structural phase transitions, which are, generaly speaking, characteristical for simple and mixed phosphates (for example /8/).

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